ELECTRON IMPACT DISSOCIATIVE EXCITATION AND IONIZATION OF MOLECULAR IONS

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The study of dissociative collisions of electrons with molecular ions has for decades been dominated by the examination of the process of dissociative recombination. The many published papers and monographs bespeak a very active field. The processes of dissociative excitation, dissociative ionization and resonant ion-pair formation have received less attention and are the focus of this chapter. Much of the discussion is oriented to the work the authors have been involved in; however, an effort is made to mention the bulk of all work which has been carried out, and in particular a table is presented of all of the experimental measurements of the subject processes of which the authors are aware. From the table one can observe that about 50% of the experiments have addressed ion targets that are the simplest diatomic and polyatomic molecules in nature and also that much of the early activity in this area was motivated by the efforts to achieve controlled fusion. More recently, again partly motivated by fusion efforts and partly by plasma etching and deposition, light hydrocarbon ions have been targets of investigation. One expects more activity in the future investigating halogen-bearing molecular ions. Dissociative excitation occurs through a direct excitation process to a dissociative molecular state, and recently there has been emphasis on a resonant dissociative excitation mechanism wherein the electron is captured to a bound state, and then stabilizes (as one route) to a dissociative state of the ion. Comparisons are made herein with alternate stabilization routes leading to dissociative recombination and resonant ion-pair formation. Only two direct measurements have been made of dissociative ionization, and these by the Newcastle group on hydrogenic ions. Recently, some dissociative ionization cross sections have been deduced by combining data yielding total product formation with other data for dissociative excitation only. This approach has severe limitations and highlights the need for more direct measurements of this process. A similar paucity of data exists for resonant ion-pair formation. Exemplary data are given for the various processes, and comparisons are made that show trends and emphasize mechanisms. Methods of experimental study are described in differing levels of detail. Techniques using ion storage rings, and a recent technique designed to study light fragments from dissociative processes, are emphasized.

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1. Introduction

Collisions of electrons with molecular positive ions are characterized by most of the same complexities and beauties of collisions with neutral molecules, as discussed elsewhere in this volume; they also enjoy features brought about by the Coulomb interaction between electrons and ions. Excitation, ionization, recombination and elastic scattering are all phenomena that must be accounted for in considering an environment with both electrons and ions.

Recombination, which for molecular ions is dominated by dissociative recombination, has commanded aggressive attention and creative investigation since it was first experimentally observed by Biondi and Brown in 1949. There are international meetings held relatively frequently to discuss this process, and there exist a number of recent monographs and reviews. To explore this process, the reader is thus referred to one of these references.

Excitation and ionization between bound molecular ion states induced by electron impact are also topics of interest. However, both concepts have received inadequate experimental attention (apparently there are only one and two published papers respectively on each of these).

Here the discussion is limited to dissociative excitation and, to a lesser extent, dissociative ionization. Though the current activity is far less intense in these areas than in recombination, the physics of electron-impact dissociation of molecular ions is an area of active investigation that has received attention beginning more than 30 years ago. In this paper we try to give an overview of work that has been done over the years with brief descriptions of the methods used to obtain results. However, the major focus is on recent work in which the authors have been involved, which includes crossed beams experiments in our laboratory to investigate light fragment ion production and also merged beams experiments in ion storage rings.

1.1 The Processes

The kind of processes we consider in this paper can be represented as

\[ \begin{align*}
XY'(B) + e &\rightarrow XY'(D) + e - X + Y^* + e + \epsilon_{DE} \quad (a) \\
XY'(B) + e &\rightarrow XY''(D) + 2e - X^* + Y^* + 2e + \epsilon_{DI} \quad (b) \\
XY'(B) + e &\rightarrow XY''(D) \rightarrow XY'(D) + e - X + Y^* + e + \epsilon_{RDE} \quad (c) \\
XY'(B) + e &\rightarrow XY''(D) \rightarrow X^* + Y^* + \epsilon_{RIP} \quad (d)
\end{align*} \]

where \( \epsilon_{DE} \) is the kinetic energy of release (KER). The first process (a) is referred to herein as dissociative excitation (DE), the second (b) as dissociative ionization (DI), the third (c) as resonant dissociative excitation (RDE), and the final one (d) as resonant ion pair formation (RIP).

For illustrative purposes, we refer to Fig. 1 which shows with solid lines electronic potential curves of a generic diatomic molecular ion with a bound state \([XY'(B)]\), some dissociative states \([e.g. XY'(D)]\) and a dissociative ion state \([XY''(D)]\). Also shown with dotted lines are Rydberg states of the neutral molecule both bound and dissociative. A few vibrational levels are sketched in for the bound ion.

![Figure 1: Schematic potential-energy diagram for a generic diatomic molecular ion XY'(B) and some dissociative states XY'(D) and dissociative ion states XY''(D), as well as a few Rydberg states of the neutral molecule.](image-url)
1.2 Franck-Condon Transitions

Generally, for all of these cases the Franck-Condon principle can be invoked. That is, it is approximated that during an electronic transition, the nuclei remain "fixed." Thus, from the ground vibrational state, one can consider that transitions occur with product states having \( R \) separations, as shown within the shaded area of Fig. 1. This may be stated more formally by considering collisional probability for transition between the bound state and the repulsive state. This is proportional to the square of the matrix element connecting the states:

\[
|\phi|^2 = |A \int \psi_e^b V_e \bar{\psi}_e^d \chi_e^b(R) \chi_e^d(R) dR|^2 \\
= |A \int U_N(R) \chi_e^b(R) \chi_e^d(R) dR|^2 \\
= |A U_N \bar{\chi}_e^b(R) \chi_e^d(R) dR|^2 = |A U_N \bar{\mathcal{F}}_{\chi_e^d(R)}|^2 = B |\mathcal{F}_{\chi_e^d(R)}|^2 
\]

(2)

where the \( \psi_e^b, \psi_e^d \)'s are electronic initial and final wave functions, the \( \chi_e \)'s are internuclear wave functions with superscripts \( b \) and \( d \) denoting bound and dissociative states respectively, \( A \) is a constant, and \( V_e \) is the coupling term between states. Here one has assumed the Born-Oppenheimer approximation that the wave functions are separable in the electronic and internuclear coordinates, but allowing in the second line that the coupling term may be \( R \) dependent. In the last line the Franck-Condon assumption has been invoked: that \( U_N(R) \) varies slowly with \( R \) and may be taken out of the integral as an average value. The term \( |\mathcal{F}_{\chi_e^d(R)}|^2 \) is called the Franck-Condon factor. When, as is the case here, the final state is a repulsive state, the continuum wave function can to good approximation be replaced by a suitably normalized delta function, so that \( \chi_e^d(R) = K \delta(R_c) \), in which case

\[
|\phi|^2 = C |\chi_e(R_c)|^2 
\]

(3)

where \( R_c \) is the classical turning point for particles of reduced mass \( \mu \) and relative energy \( \varepsilon = K^2/\mu \). Thus, one can draw the shaded area in Fig. 1 as the region over which \( \chi_e(R) \) and also \(|\phi|^2\) have finite values for transitions to the first repulsive curve. This leads us also to the so-called reflection approximation as illustrated in Fig. 1. After transition to the product state at separation \( R_p \), the constituent particles of the molecular ion dissociate with the ultimate kinetic energy of release \( \varepsilon \). As seen from the foregoing discussion, and as illustrated in the figure, the approximate resulting energy distribution is obtained simply by "reflecting" the square of the initial vibrational wave function(s) from the final repulsive potential curve (shown for only the ground state function in the figure).

1.3 Dissociation and Kinematics

Once the transition has been made to the repulsive state, the particles move apart, finally gaining the energy \( \varepsilon \) in the center-of-mass system. In the laboratory system, the energy is shared between the product particles governed by momentum and energy conservation.

All experimental studies in this paper employ colliding beams of electrons and ions. It is important to keep in mind the large spreads in angle and energy that result from the dissociation process. The maxima occur respectively when the molecular axis is perpendicular to and aligned with the beam axis, and they characterize the challenge associated with proper dispersion and detection of the fragments.

Assume a parent ion target of mass \( M = m_1 + m_2 \) having an energy \( E \) in the laboratory system and consider kinematic parameters associated with the fragment of mass \( m_1 \). Then simple arguments lead to

\[
\tan \theta_1 = \delta_1, \quad E_1 = \frac{m_1}{M} E \\
\Delta E_1 = 4 \frac{m_1}{M} \delta_1 E, \\
\delta_1 = \left( \frac{\varepsilon}{E} \right)^{1/2} \left( \frac{m_2}{m_1} \right)^{1/2} 
\]

(4)

where \( \theta_1 \) is the angle that the dissociating particle of mass \( m_1 \) makes with the initial direction of the molecular ion, and \( \Delta E_1 \) is the spread in kinetic energy of the fragment particles of mass \( m_1 \). Thus, the apparatus must be configured to collect and detect particles diverging at angle \( \theta_1 \) and with an energy spread of \( \Delta E_1 \). Problems of collection are clearly minimized for \( m_1 = m_2 \) and by making \( E \) as great as possible compared to \( \varepsilon \). The problems are most acute when \( m_1 < m_2 \).

The technical problem is put in perspective by considering a numerical example. Assume a 7 keV beam of \( CH^+ \) ions dissociated into \( C + H^+ \) with a KER of 10 eV. Then the \( H^+ \) diverges with \( \tan(\theta_1) = 0.13 \), i.e., for every 10 cm traveled, the beam diameter has grown by 2.6 cm! The \( H^+ \) fragment beam has a median laboratory
energy of 538 eV and a spread of 282 eV— from 688 to 406 eV— a spread of 52% of the median value. Conversely, if one were looking at the C fragments then tan(θ,。”) would be only 0.01 and the energy spread only 4% of the median value of 6461 eV.

One should note that the transition probability may be dependent on the angle that the molecular axis makes with the electron beam axis. Dunn has presented selection rules for diatomic molecules that indicate the nature of such dependencies and that may be applied when considering specific transitions.

1.4 History and Status

The incentives associated with controlled thermonuclear fusion led, as far as we know, to the first theoretical efforts almost a half century ago to describe dissociative excitation of molecular ions. The object of interest was the simplest of all molecules, H₂⁺; so, to the practical motivations associated with controlled fusion were added the attractions that go with investigating very fundamental physics. Nevertheless, it was not until the middle of the 1960s that the first experiments were completed in Dunn’s laboratories using crossed electron and ion beams, and a synergistic interplay between Pock’s theory and experiment led to very good agreement between theory and experiment for this simplest of all molecular ions.

Confirming experiments were soon carried out in the laboratories of Harrison and of Dolder. Whereas the earliest experiments yielded cross sections for proton production (thus also including dissociative ionization of H₂⁺), later experiments carried out in Dolder’s laboratories separately measured dissociative excitation, dissociative ionization, and ion pair formation. Again, these follow-up experiments generally used crossed or inclined beams. One other experiment on H₂⁺ was also carried out under significantly different conditions using an unusual form of ion trap.

These early experiments were carried out using a target of H₂⁺ ions formed by high energy electron bombardment of H₂, so that all 19 vibrational levels were populated in a distribution that could be calculated using the Franck-Condon principle and which was later measured using photodissociation of H₂⁺. Homonuclear H₂⁺ has no electric dipole moment, so the vibrational levels have lifetimes on the order of 10⁻¹⁰ s, thus vibrational state populations are the same throughout the various experiments conducted at low pressures. The remarkable agreements between the various sets of experiments and between the experiments and theory are strong indications that the targets were the same (exclusive of Ref. 19) and that the vibrational level populations were indeed those measured in photodissociation. Nevertheless, considering the fundamental character of H₂⁺, as new technology has come into use in the form of ion storage rings, this ion has deservedly received renewed attention, and this will be discussed more later.

In addition to results on H₂⁺, the activities of the 1960s and 1970s brought forth results from Dunn’s group for N⁺ from N₂⁺ and for O⁺ from O₂⁺, and from Dolder’s group for various products from H₂⁺, the first polyatomic ion studied. In this latter work, efforts were made to develop a target of vibrationally “cold” H₂⁺ ions, and, in addition to production of proton fragments, production of H⁻ was also investigated.

In the 1980s, attention to DE came from entirely different groups. Results on CO⁺, on N₂⁺, and on He⁺ were reported by Mitchell’s group. Also, Gregory et al. published results on H₂O⁺ and also carried out unpublished work on CO₂⁺.

The upturn in the 1990s of activity in the field can be traced to a number of sources. Once again, controlled fusion has figured strongly, since the edge plasmas of experimental reactors contain many molecular ions, and their reactions are important in the modeling. Also, the modeling of plasma generators for etching and deposition in the electronics industry has highlighted the need for such understanding. Of course, the physics and chemistry of planetary and astrophysical atmospheres, flames, lighting, gas lasers, are likewise areas where understanding of these processes is needed. Not to be underestimated in assessing reasons for the increased activity is the fact that ion storage rings present the exciting technical capability for studying electronically and vibrationally “cold” ions. Thus, the modern needs, along with both experimental and theoretical technical opportunities, provide substantial incentives for the activity that currently characterizes the field.

2. Experimental Methods

The general approach to the study of electron-impact dissociation of molecular ions is that of implementing colliding beams of electrons and ions. All of the experiments discussed herein use variants of this method.

For particles of number densities \( N_e \) and \( N_i \) colliding with relative velocity \( v \), and producing dissociation events at a rate \( dS/d\nu \) in the elemental volume \( d\nu \), the collision cross section \( \sigma \) for the process is defined through the relation

\[
\frac{dS}{d\nu} = N_e N_i \nu \sigma
\]

(5)

The number density, \( N_e \), is related to the electric currents of the particles through the relation \( I = qe \int N(x,y,z) v_z \, dA \), where the integral is over the area in a plane perpendicular to the direction of travel and \( qe \) is the charge of the particle. Hence, by
relating the fluxes to the measured beam density distributions, \( G(x,y,z) \) and \( H(x,y,z) \), and integrating over the volume of interaction, we have

\[
\sigma = \frac{S}{\gamma_e/\gamma_i} \left( \frac{q e^2}{e I_e I_i} \right) \left[ \frac{\int G(x,y,z) dA_G}{\int G(x,y,z) H(x,y,z) dxdydz} \right]
\]

(6)

Depending upon the angle at which the beams interact, the equation can be further defined. For example, for the case of merged beams, the relative velocity is simply given by \( v = |v_e - v_i| \), and if the beams are traveling in the \( z \) direction the integrations in the numerators are simply over \( x \) and \( y \). Then, if \( R \) is the registered count rate in the detector and \( e \) is the detector efficiency, the equation becomes for merged beams

\[
\sigma(R) = \frac{R}{e I_e I_i} \left( \frac{v_e v_i}{|v_e - v_i|} \right) F^2
\]

(7)

where the so-called form factor \( F \) is given by

\[
F^2 = \frac{\int G(x,y,z) dxdy \int H(x,y,z) dxdy}{\int G(x,y,z) H(x,y,z) dxdydz}
\]

(8)

For crossed beams traveling in the \( x \) and \( y \) directions respectively, the relative velocity is replaced by \((v_e^2 + v_i^2)^{\frac{1}{2}}\) and the form factor is given by

\[
F^2 = \frac{\int G(z) dz \int H(z) dz}{\int G(z) H(z) dz}
\]

(9)

Colliding charged particle beams are beset by their own peculiar problems and these have been documented.\(^{33,34,35}\) We discuss the major ones briefly here, but emphasize their importance because they are genuine problems to which attention must be given. One typically finds rather large fragment counting rates due to breakup of the target ions on both ambient gas particles and surfaces. These are often much larger rates than those from the dissociative collisions with electrons that are being studied. Thus, it is necessary to modulate or chop the electron beam that normally does not produce background counts. However, the presence or absence of electrons can affect the background rates, and since the backgrounds are so large compared to signals, very small effects of this type will appear as anomalous “signal.”

One way in which this false signal appears is through modulation of the background by the space charge of the electron beam, i.e., the space charge potential of the electrons causes the ions (both primary and fragment) to take different trajectories and if these different trajectories change the amount of background collected, then a false signal is present. Testing for this is done by varying the electron current density and by carefully analyzing the “signals” for apparent cross section values below the energy threshold for the process being investigated. Also, testing the signals with a variety of beam focus conditions is a helpful procedure.

Another false signal may appear when the impact of the modulated beam releases gas from the collector surface. Since some background is directly due to the breakup of target ions on background gas, modulation of the pressure will give rise to an accompanying modulation of the background, thus an anomalous signal. This effect must carefully be tested for and eliminated. Often it can be detected by varying the frequency with which the electrons are modulated, since the amplitude and phase of the modulated false signal are affected by the frequency.

Still another false signal can arise if the electron energies are high enough to ionize the background gas. Slow ions so created may be trapped in the space charge well of the electron beam, thus giving another class of colliding partner that may cause breakup of the ions under study. Since these trapped ions come and go with the electrons, the fragments thus created appear as a modulated false signal. A high modulation frequency and low background pressure can eliminate this problem, and variation of these parameters can help detect the presence or absence of the effect.

As in any experiment and measurement, the proper functional dependencies shown in Eqs. (7)–(9) must be verified. Finally, as already emphasized from the beginning of this paper, strict attention must be paid to ensure that all fragment ions under study are collected or accounted for. This is a special problem at the low ion velocities encountered in more traditional apparatus, but also needs attention in the work done on ion storage rings.

Energies of the respective particles in the beams are not simply obtained by reading voltages applied to cathodes or ion sources. There are contact potentials,
plasma boundary potentials, and other effects that come into play, and the energies must be calibrated with a variety of methods depending upon the beams' configurations.

2.1 Crossed Beams I

The crossed beams setups used in the early H$^+$ measurements$^{6,12,14,15}$ were generic in character. Each employed magnetic sector fields to obtain a pure ion target and electrostatically focused electron beams at right angles to the ion beams, and each employed moveable slit scanners to determine F in Eq. (9). The experiments at JILA$^{6,12}$ and Newcastle$^{13}$ employed ion sources that should have yielded vibrational states as measured in photodissociation. Both the experiments at JILA and at Culham$^{14}$ measured product elastic currents as signals, while the Newcastle experiments used single-particle counting. The Culham and Newcastle experiments employed magnetic separation of the fragment signals, while the JILA experiment used electrostatic separation.

In all of these experiments the investigators displayed exemplary care in obviating the problems associated with colliding charged beams measurements, and all went to unusual lengths to demonstrate correct functional dependencies. The agreement between all of the measurements is good. The agreement between the JILA and Newcastle results is exceptional, especially when proper account is taken of that fact that at JILA the quantity measured $\sigma_{pe} + 2\sigma_{p2}$, while at Newcastle the measurement was $\sigma_{pe} + \sigma_{p1}$. One might consider these sets of experiments and their results as paradigms in the area of electron impact dissociation of molecular ions.

2.2 Crossed Beams II

In the flurry of the recent activity that surrounds molecular-ion dissociation, the crossed beams configuration has again emerged. Two versions are now in use, one of which is similar to those previously used at Culham and Newcastle, while the other is a rather radical departure and is aimed at detecting and measuring only light fragment ions from a dissociative collision, e.g., D$^+$ from CD$_4^+$ as discussed in Sec. 2.3.

The crossed beams apparatus at Oak Ridge National Laboratory (ORNL) that was configured primarily for electron-impact ionization of highly-charged ions was turned for a time in the late 1980s to the purpose of molecular-ion dissociation measurements$^{16,17}$ The magnetic sector, which is the dispersive device in these experiments, separates particles according to momentum/charge ratio. In ionization measurements, the momentum stays fixed, but the charge changes. In dissociation measurements the charge and (approximately) the velocity remain the same, but the mass and thus the momentum of the fragment is different. Thus, dispersion is easily accomplished. The difficulty lies in the broad angles and energies discussed in Sec. 1.3. Hence, the technique is limited to fragment ion masses not far from that of the parent ion. One difference with the crossed beams apparatus at Culham and the one at Newcastle was the use at Oak Ridge of a magnetically confined electron gun. This adds additional complications to the trajectories of the primary and fragment ions, since they are bent differently in the magnetic field of the electron gun, and compensation with electric field deflectors cannot be exactly the same for both types of ions. The ORNL apparatus has now been reconfigured with an electrostatically focused electron gun, and further studies of electron-impact dissociation of molecular ions yielding "heavy" fragments are planned$^{18}$.

Quite recently the group at Louvain-la-Neuve$^{19}$ used crossed beams with magnetic dispersion of fragments to measure dissociative ionization of molecular ions when the fragment ion is doubly charged. They incorporate the animed beam method where the electron beam is swept through the ion beam at constant velocity, a technique that avoids a direct measure of the form factor $f^*$ in Eq. (9). An electrostatic analyzer is included after the magnetic field for energy as well as momentum dispersion.

2.3 Crossed Beams III

As noted earlier, a quite different method must be used to collect and quantitatively measure the number of light fragment ions in dissociative collisions. This is one of the approaches the authors of this chapter currently employ, and significant emphasis is given to this method in this chapter. The discussion here closely follows that given elsewhere$^{20}$.

The JILA crossed beams apparatus$^{21}$ was modified, and a new detector chamber and new dispersion and detection systems were implemented, as shown in Fig. 2. This represents one of the major departures from the past for these studies, so a more detailed description is provided here, including some procedures for obtaining the experimental data.

Ions are produced in a gas-fed commercial hot-cathode-discharge ion source$^{22}$ held at +7 kV. They are extracted through a hole in the anode, formed into a beam, mass analyzed with a sector magnetic field, and led through stages of differential pumping into the collision chamber (10$^{-7}$ Pa). Source conditions were empirically optimized for maximum beam intensity. The target ions produced in this way could have been in vibrationally and/or electronically excited states, it was not possible to control or calculate their distributions.
A magnetically confined electron beam\textsuperscript{41} intersects the ion beam at 90°. The collimating magnetic field of the electron gun was reduced from 0.02 T to 0.006 T to cut down the dispersive deflection of different ions in this field. The complications associated with this e-gun magnetic field deflection are exacerbated for light ions, so cutting it down was important. However, with this lower magnetic field the maximum energy at which the electron gun delivers a well-defined beam is limited to about 70 eV. The remaining bending of the ions in this field was partially compensated for by electrostatic deflection immediately before and after the collision region. The electron beam was chopped at 1000 Hz, and the histogram memories where the signals were accumulated were gated to record counts with electrons on and off in order to separate the true signal produced in electron-ion collision from background events. A scanning slit probe was located in the center of the collision box to measure spatial profiles of both the electron and ion beams.

Immediately after the collision region, both target and fragment ions experience strong acceleration (by typically 5000-7000 volts) in the first part of a cylindrical lens system (CLS) designed to collect, accelerate, and transport the fragment ions of interest into the analyzer chamber. The lens system consists of five cylinders, a drift tube, and three more cylinders. Cylinders are 50 mm long and 50 mm in diameter, some of them being segmented lengthwise so that vertical and horizontal deflections are also available. The analyzer consists of two 45° electrostatic analyzers. The first analyzer separates studied fragment ions from other products and from the primary beam. It deflects the selected ion products onto a position sensitive detector (PSD) consisting of a pair of microchannel plates with a sensitive diameter of 40 mm and a resistive anode. The detector is mounted on a linear motion feedthrough with linear travel of 50 mm. Counts from the PSD are registered according to the x-y position into two separate time-gated pixel arrays of 256 x 64 pixels respectively and stored in two separate histogram memories registering background and background + signal at each of the 16,384 positions in the respective time gates.

The parent ion beam largely retains its initial collimation and energy spread and is not greatly affected by voltages applied at the CLS, but the first 45° analyzer deflects the beam somewhat. The second 45° analyzer and two sets of horizontal deflectors that follow are used to redirect the primary beam and heavy fragments out of the analyzer chamber toward the electrically isolated smaller chamber. This additional chamber is used to "bury" the primary beam, and it is also used as a large ion collector. It contains an inline movable slit (which can be interchanged with a small Faraday cup), horizontal deflectors, and a microchannel plate followed by a fluorescent screen, which are used as diagnostic tools.

From the point of collision, the particle transport and dispersion were modeled using a three-dimensional trajectory modeling program\textsuperscript{42} (SIMION) to investigate the capability of the apparatus to collect fragment ions under investigation and to separate these ions from the main beam and from other fragment ions. The model calculations assumed the breakup of simple deuterated ions CD\textsubscript{n}+ (n=1-5) traveling at a fixed incident velocity (corresponding to 7 keV) into light fragments D\textsuperscript{+} (D\textsubscript{2})\textsuperscript{+} and unspecified other fragments. The excess kinetic energy in the simulations was chosen to be not more than 10 eV per fragment ion. The relevant broad ranges of transverse and longitudinal energies were inserted in the modeling, and conditions were determined by which desired particles would be fully collected. Both the transport and analyzer parameters vary as the target ion or detected fragment ion changes. The width of the fragment ion distribution in the vertical direction (y direction at PSD) is due to the angular spread of the fragment ion beam, to focusing conditions, and to the size of the primary beam, and has an extra deflection in one direction due to the vxB field in the collision region. The width of the fragment ion distribution in the horizontal direction (x-direction at PSD) results from angular spread, focusing, and beam size plus dispersion in the analyzer due to the energy spread (forward-backward) of the fragment beam.

Examples of the x-y signal distributions on the PSD of D\textsuperscript{+} fragment ions from CD\textsuperscript{2} is shown in Fig. 3. The distribution is relatively narrow in the y-direction, while in the x-direction (direction of PSD movement) it is broader. For some fragments (though not for D\textsuperscript{+} from CD\textsuperscript{2}) it can become so great that significantly less than 100% of the fragments are detected at that PSD position. In such a case, translating the PSD to a different position is necessary, and a procedure for summing up the signal at different PSD positions has to be applied. Motion of the PSD is achieved by micrometer adjustment so that reproducible and accurate settings are possible, thus
making such a summation procedure reliable. Changing the target ion so that the fragment is even lighter compared to the target, the distribution on the PSD in the x-direction becomes wider, while the signal distribution in the y-direction does not change significantly.

As expected from the angular and energy spreads of the fragment ions under investigation, there are no small focus points for the particles. Hence, the detector is large and open to receive all investigated fragment ions. This makes it vulnerable to backgrounds of different origins. Ion background counts can arrive at the detector due to ion breakup on background gas and on surfaces and edges of electrodes. Photon background counts can arise from the beams’ hitting the collector or electrodes. As already noted, the backgrounds are in principle separated by chopping the electron beam at 1000 Hz and appropriately gating separate histogram memories. However, the backgrounds, for reasons just noted, were particularly severe and had to be minimized — not only to obtain acceptable signal to background ratios in order to get adequate precision in a reasonable time, but also to cut down the possibility of space-charge modulation of the background giving rise to a “false signal” as discussed at the beginning of Sec. 2.

To resolve the background origin, a time-of-flight technique was employed. A chop pulse applied to a horizontal deflector near the ion source exit provided the start pulse to a time-to-amplitude converter, and the pulses from the PSD generated by interaction of the primary beam with residual gas and/or surfaces (background) are used as the stop. The arrival time spectrum, acquired in a multichannel analyzer, consists of two close narrow peaks and one broader peak. The first two peaks were identified as coming from the dissociation of the parent ion, most likely in collisions with the surfaces near the collision box. The background count rate did not change significantly when the pressure in the beam transport line and collision chamber changed by a factor of 10, and thus surfaces were the main source. The third peak is due to photons produced by the parent beam hitting surfaces inside the isolated ion-collector chamber and traveling back directly or via reflection to the PSD. Coating the small chamber and all surfaces that can reflect photons toward the PSD with graphite helped to almost eliminate the background noise coming from photons. However, background remains a problem; its level depends on the ion target and which fragmentation channel is investigated.

The data-taking procedure for a given fragment typically begins with setting the PSD position and all voltages upstream from the collision region to values consistent with the SIMION trajectory modeling. The primary ion beam is then tuned to achieve minimum background, and the form factor $F$ is measured at the chosen electron energy. Collection of the data in two channels continues until adequate statistical uncertainties are reached. When necessary, the position of the PSD (in the x-direction) is then changed (usually 10 mm) and the collection of the data repeated. The signal detected at the new PSD position is a combination of part of the signal measured at the previous PSD position (“overlapped” signal) and the signal that was missed at the previous position. Changing the PSD position is continued as long as a detectable signal is collected (usually three positions covering the linear motion of 50-60 mm are enough to collect all signal ions). Final data at a given interaction energy is then obtained by summing up the total signal at one PSD position and by adding the “missing” signal for that position as measured at other PSD positions. The electron energy is then changed and all procedures repeated.

The efficiency of the PSD was measured in a separate experiment by directing a very small current (typically a few femto-amperes) of fragment ions (with energy equal to the fragments under study) alternatively onto the PSD and into the ion collector where the current was measured with a vibrating-reed electrometer. The ratio of ion number so determined yielded the efficiency.

The electron energy scale was calibrated by measuring the cross section for single ionization of N$^+$ ions, linearly extrapolating it to zero, and ascribing the intercept as the spectroscopic threshold energy$^{43}$ of 29.6 eV.

2.4 Merged Beams I

In order to take advantage of the kinematic benefits of merged beams to obtain low interaction energies to measure cross sections for dissociative recombination of electrons with molecular ions, McGowan et al.$^{44}$ developed the Merged Electron-Ion Beams Experiment (MEIBE) at the University of Western Ontario. Electrons of velocity $v_e$ from an electron gun were introduced into a region of uniform crossed electric and magnetic fields. Here the electrons execute trochoidal motion with a drift velocity equal to $\mathbf{v} = (\mathbf{E} \times \mathbf{B})/B^2$ in the x direction perpendicular to the direction (z)
of the initial velocity. After an integral number \( n \) of cyclotron periods, the electrons have moved a distance \( r(2\pi n/\omega) \) in the \( x \) direction, are at the same height \( y \) and have advanced \( \nu_x(2\pi n/\omega) \) in the initial \( z \) direction. At this point, the velocity of the electrons is again simply \( \nu_x \) as the electrons leave the region of crossed fields. Ions of mass \( M \) are introduced along this same new axis, and the electrons and ions continue co-linearly merged for some distance until another region of crossed fields is introduced, and the electrons are again made to drift to a new axis where a Faraday cup is located to collect the electrons. A probe is introduced at several fixed positions in the merge region to measure the beam density distributions. A schematic diagram of this arrangement is shown in Fig. 4.

![Schematic diagram of the MEIIE experimental approach at the University of Western Ontario](image)

**Figure 4:** Schematic diagram of the MEIIE experimental approach at the University of Western Ontario (used with permission).

Ions continue on their path until they encounter a field that bends them into a collector where the ion current is measured. Neutrals that result from recombination of an electron and an ion continue in straight trajectories onto an energy sensitive surface barrier detector where (independent of the number of neutral fragments resulting from dissociative recombination) a pulse height characteristic of the full ion energy \( E \) is registered. Almost as a bonus, neutral fragments of mass \( m_i \) that result from dissociative excitation also continue to the detector (the ion fragment is bent into a new direction) where they are registered with a pulse height characteristic of the fractional energy \( (m_i/M)E \) of the fragment neutral. Thus, Mitchell et al., capitalized on this to obtain measurements of \( DE \) for several molecular ions. Generally, as in the crossed beams experiments, the ions have a flight time of a few microseconds from the ion source to the interaction region so that the ion targets are “hot” vibrationally and perhaps electronically. However, in some cases these investigators went to extra efforts to obtain vibrationally relaxed ions before they left the ion source.

It should be pointed out that in the MEIIE approach a reduction of the longitudinal electron temperature \( T_z \) is obtained by kinematic effects. To obtain a reduction in the transverse electron temperature \( T_x \), using trochoidal analyzers, one would normally expect it necessary to implement limiting slits. The MEIIE apparatus has no such slits or apertures, yet the authors observe apparent features in dissociative recombination cross sections that lead them to deduce a \( T_x \) (\( < 100 \text{ K} \)) much lower than the cathode temperature (\( > 1000 \text{ K} \)). This remains an enigma.

### 2.5 Merged Beams II: Storage Rings

Perhaps one of the most profound advancements in the field of electron-ion collision studies has come through the development of ion storage rings. The rings offer high luminosity, long storage times so that internal states can decay or be manipulated, excellent energy resolution, and high detection sensitivity. Four rings have been built and used for low energy electron-molecular ion studies: ASTRID\( ^{47} \) in Aarhus, Denmark; CRYRING\( ^{48} \) in Stockholm, Sweden; TSR\( ^{49} \) in Heidelberg, Germany; and TARN\( ^{50} \) in Tokyo, Japan. In this discussion we will focus primarily on the CRYRING in Stockholm, since both authors have collaborated on molecular ion experiments there.

An artist’s view of CRYRING is shown in Fig. 5. Ions from a variety of ion sources can be injected into the ring. Among the sources are included the CRYSIS which is an electron beam ion source to obtain very highly charged ions. For molecular ions of interest here, two sources have been primarily used. The most common one is a simple hot cathode discharge source (e.g., MINIS in Fig. 5) operated at a few milli-Torr of whatever gas produces ions under study. On at least one occasion a hollow cathode higher pressure discharge source was used to obtain vibrationally colder ions of diatomic gases (\( \text{N}_2^+ \) in this case), since even with seconds of storage time homonuclear ions will not vibrationally relax.

Ions are accelerated out of the ion source by about 40 kV, then further accelerated in an RFQ (radio frequency quadrupole) to about 300 keVamu and injected into the ring. In the ring the ions can be further accelerated (acceleration system in Fig. 5) to a maximum energy characteristic of the magnetic rigidity of the ring. For CRYRING the maximum energy is given by the expression \( E_{\text{max}} = 96 (q/M)^2 \text{MeVamu} \), where \( q \) is the charge of the ion and \( M \) is the mass in amu. Ions are bent and focused with a periodic structure of bending and focusing magnets, and there are devices for beam diagnostics and measurement. The background gas density of about \( 7 \times 10^4 \text{ cm}^{-3}(2 \times 10^{-11} \text{ Torr}) \) is low enough to insure a reasonable lifetime of the ions in the ring. However, this density is the lifetime-limiting factor of the ions, and as the ions become
more massive and slower the charge transfer and ion-gas breakup cross sections become large enough that the storage lifetime eventually becomes prohibitively short. Ion mass around $32$ for singly charged ions probably approaches the upper limit for what is possible to use for electron-molecular ion experiments in CRYRING for this and other reasons (e.g., having an energetic enough electron beam to get reasonable current). On the other hand, Kr$^+$ has been successfully stored and used for spectroscopic experiments, and of course highly-charged ions are a totally separate story as the $q^2$ factor on $E_m$ indicates.

\[
f(v_e) = \frac{m_e}{2\pi kT_{e1}} \left( \frac{m_e}{2\pi kT_{e1}} \right)^{1/2} \exp \left( -\frac{m_v v_e^2}{2kT_{e1}} - \frac{m_v v_e^2}{2kT_{e1}} \right)
\]

where $m_e$ is the electron mass, and the subscripts $\parallel$ and $\perp$ respectively identify the parallel and perpendicular temperature $T$ and velocity $v$. The temperatures at the cathode are of order $0.1$ eV, and the parallel temperature is contracted by the longitudinal beam acceleration to $0.1$ meV or less. The perpendicular temperature is reduced by a scheme first proposed and demonstrated by Danared et al.$^{51}$ wherein the electron beam adiabatically expands from the cathode to the interaction region, i.e., the cathode is located in a region of strong longitudinal magnetic field and the interaction region is a region of much-reduced field. By this expansion technique, the transverse temperatures have been reduced to the order of $10$ meV. Efforts are currently underway to implement superconducting magnets for the field in the cathode region and temperatures of the order of less than $1$ meV are anticipated.

For molecular ions, this kind of super energy resolution has been used primarily for measurements on dissociative recombination and to this point has not proved useful nor necessary for studies of DE with storage rings. Also, it should be pointed out that the cooling of the ion beam is not a necessity in either the DR or DE experiments. In fact, for singly charged ions, as the mass increases above $20$ amu or so, the mass disparity between electrons and ions leads to such poor momentum transfer that cooling of the ion beam cannot take place readily within the lifetime of the beam. The momentum spread of the uncooled ion beam then does contribute to the center-of-mass energy spread, but not so seriously as to be a limiting factor.

The space charge of the electron beam lowers the beam energy within the beam and by an amount dependent on the position within the beam. This is partially offset by the fact that the electrons ionize the background gas, and the slow ions formed tend to get trapped within the space charge well of the electron beam. The laboratory energy of an electron in the space charge well of the electron beam is given by:

\[
E_e = eV_e - \frac{1}{eV_e} \frac{me^2c^2}{ev_e} \left[ 1 + 2\ln \left( \frac{b}{a} \right) - \left( \frac{r}{a} \right)^2 \right] + \xi(E_e),
\]

where $V_e$ is the true difference in potential between the cathode and the drift tube including contact potentials, $I_e$ is the electron current, and $r_e$ is the classical radius of the...
electron, and $E_2$ and $v_e$ are the laboratory electron energy and velocity, respectively. Here $b$ and $a$ are respectively the radius of the beam tube and the beam, $r$ is the distance from the center of the beam, and $\xi(E_2)$ is the space charge neutralization by trapped slow ions and depends upon electron energy because the cross section for ionization of the background gas is energy dependent. One can suppose that this term is simply proportional to the cross section $\sigma_1(E_2)$ for ionization and becomes $\xi(E_2) = B_0 \sigma_1(E_2)$. Since $r$ is greater for an uncooled beam, the energy of the electrons will have an energy spread characteristic of the range of $r$. However, numerical evaluation of this shows that this is an inconsequential effect. Hence, on all counts, for these experiments it does not matter that the ion beam is not "cooled" by the electrons.

For a uniform electron beam of area $A_e$, Eq. (8) simply becomes $A_e/L$. In this case, for storage rings, Eq. (7) can be used to obtain the rate coefficient $\alpha_{DE}(E_e)$ for dissociative excitation

$$\alpha_{DE}(E_e) = \langle \sigma_{DE}(E_e) \rangle v_e = \frac{R}{C \left( \frac{1}{n_e N_i} \right) \left( \frac{C}{L} \right)},$$  \hspace{1cm} (12)

where $n_e$ is the electron density, $N_i$ is the total number of stored ions, and $C$ is the circumference of the ion trajectory in the ring.

In line with the merge path and named "0° Detector" in Fig. 5, detectors of neutral particles are mounted. For DE the detection of neutral fragments has been the primary mode of operation, though some work has been done at ASTRID detecting ion fragments. As in Sec. 2.4, surface barrier detectors are used in the 0° chamber and they give pulses out with pulse height proportional to $(m/M)E$. Since the efficiency of a surface barrier detector is essentially unity for detecting particles with the energies involved here, Eq. (12) can then be used to deduce the DE rate coefficient and hence the cross section, provided that $R$ is the count rate due to DE. As noted at the beginning of Sec. 2, however, there will be many pulses of this pulse height arriving at the detector which are due to gas breakup. This background $B_0$ is normally used as a monitor of the number of ions that is decaying exponentially, since the pressure in the ring is quite constant. Thus, with no further complications, one could measure in a multi-scaler time spectrum both the quantities $K R_0 e^{-\alpha t}$ and $K R_n e^{-\alpha t}$ when the electrons are alternately on and off respectively. Subtracting, and using the known parts of $K$ from Eq. (12), one can get the cross section. However, there are additional complications, since each time the electrons are switched on they ionize the background gas. As discussed at the beginning of Sec. 2, the slow ions so formed flow to the center of the space charge well which is formed by the electron beam and then

out the ends, exponentially attaining an equilibrium concentration in the center of the electron beam precisely where the ion beam is traveling. Thus, in analyzing the data, one must take the data for only a very short time after turning the electrons on before the trapped ion concentration has had a chance to build up. For most studies so far this effect has been relatively small. This problem as well as the additional complication introduced by the $\xi(E_2)$ term in Eq. (11) can be eliminated by fast-chopping the electron beam as discussed at the beginning of Sec. 2. So far this has not been technically feasible at CPYRING, but it has been done at TSR and ASTRID.

3. Cross Sections

It is not our purpose to give a data compilation of cross sections. Nevertheless, before proceeding to a discussion of some features of DE cross sections, it is useful to present a summary in Table 1 of measurements that have been performed along with an indication of the method of measurement and the quantities measured.

It is clear from the table that hydrogen in various molecular and isotopic forms has been the object of about 50% of the entries in the table. This is well justified from the point of view of the fundamental character of this species; $H_2^+$ is the simplest of all molecules and $H^+$ is the simplest of all polyatomic molecules. One could carry it a step further and note that HD$^+$ is the simplest heteronuclear molecule. In addition, we have already emphasized the practical importance of these species in controlled fusion and in astrophysics.

In Sec. 3.1, we look at DE [process I(a) of Eq. (1)] and highlight important features coming from the hydrogen investigations while emphasizing the importance of the synergism with theoretical work. We then look in Sec. 3.2 at DE of the CH$^+$ family, to emphasize some systematic trends for which we have no explanation. The DE data for other ions in Table 1 are somewhat nondescriptive and are not further discussed. In Sec. 3.3 cross sections for dissociative ionization [process I(b) or DI] are described, both those measured directly and those deduced from a combination of other experiments. Section 3.4 deals with resonant dissociative excitation [process I(c) or RDE, emphasizing those cases that are most striking and demonstrative. In Sec. 3.5 the limited data for resonant ion pair formation [process I(d) or RIP] are described.

3.1 Dissociative Excitation: Hydrogen

One of the most interesting features associated with DE was demonstrated in a synergism between theory and experiment more than 30 years ago. Figure 6 illustrates the prediction by Peck$^{31}$ that there is a factor of about 300 difference between the DE
cross section from \( v = 0 \) and \( v = 18 \) for the \( 1s_\sigma^2 - 2p_\sigma \) transition. He noted that the
figure shows "the influence of the initial vibrational state and clearly indicates the
necessity of having accurate knowledge of the population of vibrational states
prevalent during a measurement to make a prediction of the effective cross section." Fortunately, the long vibrational lifetime (\( \sim 10^7 \) s) and good knowledge of the \( H_2 \) and
\( H_2^+ \) potential curves make it possible to obtain ionic targets for which such vibrational
state knowledge is possible. Thus, experimenters were able to use Franck-Condon (F-C)
factors\(^{20}\) to define the vibrational populations \( p_v \) and demonstrate excellent
agreement with the theory. (In fact, the populations were shown\(^{21}\) to be just slightly

---

**Figure 6:** The total cross section \( Q_c \) for electron excitation for transition \( 1s_\sigma^2 \rightarrow 1p_\sigma \) in \( H_2 \), for all bound states
of the ground state of \( H_2 \), shown as a function of the relative velocity \( V_0 \) of the collision, in atomic units. The
upper scale is the energy in eV of electron colliding with a stationary hydrogen-molecule ion (used with
permission).

---

**Table 1:** Listing of cross section measurements for DE of molecular ions by electrons.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Products</th>
<th>( N_d )</th>
<th>( \sigma ) upper limit</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2^+ )</td>
<td>( \text{H}^+ + \text{e} )</td>
<td>+</td>
<td>10 - 20 (90)</td>
<td>6, 12, 13, 15</td>
</tr>
<tr>
<td>( \text{H}_2^\cdot )</td>
<td>( \text{H}^+ + (\text{H}^+ + \text{e}) )</td>
<td>+</td>
<td>10 (90)</td>
<td>16</td>
</tr>
<tr>
<td>( \text{H}_2^\cdot )</td>
<td>( \text{H}^+ + (\text{H}^+ + \text{e}) )</td>
<td>X</td>
<td>10 - 20 (90)</td>
<td>17</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>( \text{H}^+ + \text{e} )</td>
<td>T</td>
<td>Large</td>
<td>18</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>( \text{H}^+ + \text{e} )</td>
<td>M</td>
<td>30 - 40 (10)</td>
<td>19</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>( \text{H}^+ + \text{e} )</td>
<td>50 + (10)</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>( \text{H}^+ + \text{e} )</td>
<td>R</td>
<td>20 (10)</td>
<td>54</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>( \text{H}^+ + \text{e} )</td>
<td>R</td>
<td>50 (10)</td>
<td>55</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>( \text{H}^+ + \text{e} )</td>
<td>R</td>
<td>20 (10)</td>
<td>56, 57</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>( \text{H}^+ + \text{e} )</td>
<td>R</td>
<td>20 (10)</td>
<td>58</td>
</tr>
</tbody>
</table>

- Known vibrational populations according to
  photodissociation measurements and approximately as
  F-C factors.
- Same as above on vibrational levels coincidence.
- Same as above on vibrational levels, scavenger detector.
- Same as above on vibrational levels.
- Unknown vibrational populations, lower than above
  experiments. Difficult experiment to interpret.
- Same first 4 comments on vibrational levels, unknown.
- Unknown distribution of vibrational levels.
- Normalized with \( \sigma^2 \) error, hence, divide data by 2.
| Unknown distribution of internal states in target | 38 | [0] 20 09 0 | + | Other | CD | CH |
| Unknown distribution of internal states | 69 | [0] 10 08 0 | + | Other | CO | CO |
| Combination of Bohr states | 67 | [0] 10 20 0 | + | Other | CO | CO |
| Combination of Bohr states | 72 | [0] 25 20 0 | + | Other | CO | CO |
| Rapid rise from ion source to collision region gives | 0 | [0] 30 09 0 | | Other | CO | CO |

| Relaxed ions, D1 normalized with x2 factor | 56 | [0] 10 00 0 | + | Other | OH |
| Unknown distribution of excited states in target | 63 | [0] 10 04 0 | + | Other | O |
| Combination of data, R2, 23, 65, etc. for DI | 69 | [0] 10 10 0 | + | Other | N |
| Some vibrational excitation, v = 0 - 3 | 65 | [0] 10 05 0 | + | Other | N |
| Internal excited unknown, resonances reported | 68 | [0] 10 04 0 | + | Other | N |
| Unknown distribution of excited states in target | 20 | [0] 10 04 0 | + | Other | N |
| Relaxed ions,Neutral R1 peak in the channel near 34 | 64 | [0] 10 30 0 | | Other | H |
| Internal excited unknown, resonances reported | 63 | [0] 10 04 0 | | Other | H |
| Peak at 6 eV, Neutral R2 peak in 2 channel | 62 | [0] 10 30 0 | | Other | H |
| Low internal excited, large R1 peak in 2 channel | 19 | [0] 10 30 0 | | Other | H |
| Low internal excited, resonances reported | 60 | [0] 10 04 0 | | Other | H |
| Low internal excited, resonances reported | 56 | [0] 10 04 0 | | Other | H |
| Expansion of box for collision region | 20 | [0] 10 00 0 | | Other | H |
| Two unimolecular reactions, etc. | 25 | [0] 10 00 0 | | Other | H |
| Energy ion 67 vibrational relaxed ions | 22 | [0] 10 00 0 | | Other | H |
different in later work using photodissociation). The first experiments detected and measured proton production from the collision so that the respective theoretical curve for comparison had to be constructed according to $\sigma_T = \Sigma_p \rho_n \sigma_i$, where $\rho_n = \sigma_i(2p\sigma_n) + \sigma_i(2p\pi) + \sigma_i(2s\sigma_n) + no_w$, the ionization cross section being included $n$ times depending upon how many protons are detected from the ionization ($n$ equals 1 or 2 depending upon whether the protons are counted or current measured).

Figure 7 shows the results of many of the experiments on $\text{H}_2^+$ and $\text{HD}^+$. For purposes of verifying the vibrational state dependence, consider first the solid curve that is constructed from the various calculated components as just described with the $\rho_n$ as determined by von Busch and Dunn. The dotted curve is the theoretical curve for $\nu = 0$ (without any consideration of RDE). The data of Dunn and Van Zyl+ (open circles), Dance et al. (open triangles), Peart and Dolder (open squares) and Younis and Mitchell+ (+’s) are all for target $\text{H}_2^+$ ions created by high energy electron bombardment in a low pressure ion source, so the vibrational populations should be much the same and as given by von Busch and Dunn or as F-C factors. We note excellent agreement of the data with the constructed theory curve and with each other, thus verifying the predicted strong vibrational state dependence of the cross section.

It should be noted that the error bars for Refs. 6, 14, and 15 represent 90% confidence limits, while those for Ref. 53 represent 63% confidence limits and should be multiplied by 1.7 to be comparable to the others. Error bars are not put in the figure for the data from Ref. 55, but a statement in the paper indicates a ±20% uncertainty at 63% confidence level (or ±34% at 90% CL).

The theoretical calculations do not show a strong vibrational state dependence for electronic transitions other than to $2p\sigma_n$. Thus, while this early work clearly demonstrates the occurrence of a strong influence of vibrational excitation on DE cross sections, it does not follow that all transitions in all molecular ions will also be so sensitive.

With the advent of storage rings, it is now possible to store $\text{HD}^+$ for long enough times that the vibrational levels should relax to $\nu = 0$. This was done primarily to measure DR but DE was also measured as a “bonus.” Also, with $\text{H}_2^+$ stored, some manipulation of vibrational levels via laser photodissociation was carried out and both DR and DE were observed and analyzed. In the case of $\text{HD}^+$, involvement of RDE was evident and noted. Attention as far as comparison with theory is concerned was concentrated on comparing with the RDE calculations of Takagi, and the agreement is reasonable. The data from ASTRID are shown by the inverted open triangles in the figure, and some similarity to the dotted curve is noted at energies greater than 8 eV. Below this, the RDE contributions are evident, and Takagi’s theoretical values are also represented in this region by the heavy solid curve. The TSR values are shown in this region as a dashed curve. Other, more demonstrative
experimental studies used the deuterated species as the target for technical reasons; in the discussion that follows, the generic form will be used except when referring to specific data. Since the electronic processes should be much the same, there should be little difference except when RDE is involved.

The CH⁺ ion is the simplest member of this group, and measurements have been conducted using both crossed beams with CD³ and with a storage ring \(^{56,70}\) using CD⁺ and CH⁺. In the crossed beams experiment, D' was detected, while in the Heidelberg storage ring (TSR), neutral C was detected. Results are shown in Fig. 8, with the points representing the crossed beams data (90% CL) and the curve representing the ring data (no error bars shown, but data have uncertainties in the ±50% range at 63% CL). It is seen that the data are well up to an energy of about 30 eV. Since the detection of D⁺ will also include the DI process (Eq. 1b), and detection of neutral C does not include DI, it is natural to ascribe the difference past 30 eV to DI. This will be discussed further in Sec. 3.3.

**Figure 7:** Comparison of cross sections for the dissociative excitation of H₂⁺ examples of RDE will be discussed later.

In the Astrid experiment, the H₂⁺ ion target was "cleaned" by photodissociation of essentially everything except v = 0 and v = 1, but the specific populations of these levels could not be specified. The data are shown in the figure by the solid inverted triangles. The peak that could be established from these measurements relative to the vibrational dependence of the DE cross section was "the data may indicate that the DE cross section at 10 - 20 eV involving ions in the first vibrationally excited state is larger than that involving ions in the vibrational ground state." It must be concluded that storage ring technology presents further opportunities to explore DE of hydrogen molecular ions and the isotopomers.

### 3.2 Dissociative Excitation: CH⁺ (CD⁺)

This group of ions is of particular importance and interest because of its occurrence in the edge plasmas \(^{32}\) of Tokamaks, in dense interstellar clouds, \(^{76}\) in the ionospheres of giant planets and their satellites, \(^{77}\) and in comas of comets. \(^{78}\) Most of the DE

**Figure 8:** Absolute cross section for electron interaction with CD⁺, producing D⁺. Solid points are from Ref. 38 with 90% CL. The solid curve illustrates the data from Ref. 36.

Dissociative excitation of CD⁺ + e → D⁺ + products has been measured \(^{72}\) with crossed beams for n = 1-5. There is remarkably little to say about any of the individual cross sections, but as a group there are some trends which should be noted. Figure 9 shows this group of cross sections plotted versus interaction energy. The conspicuous
3.3 Dissociative Ionization

Apparently the only direct measurement of DI for a molecular ion is that of Peart and Dolder\textsuperscript{17} for \( \text{H}_2^+ \), the reaction then being \( \text{H}_2^+ + \text{e} \rightarrow \text{H}^+ + \text{H} + 2e \). The crossed beams approach was used with momentum dispersion of the fragment ions. A CsI(Tl) crystal and photomultiplier were used as the detector so that the almost simultaneous arrival of two protons formed from DI gave pulses that could be resolved from those due to single protons formed by DE. Their data are shown in Fig. 10 along with a Gryzinski-type calculation by Alsmiller.\textsuperscript{79} Peart and Dolder concluded that there was probably no large dependence of the cross section on vibrational level of the target ion.

![Figure 9: Absolute cross section measurements for \( \text{D}^+ \) fragment ion production from \( \text{CD}_n^+ \): \( \bullet \), \( \text{CD}^+ \); \( \bigcirc \), \( \text{CD}_n^+ \); \( \triangle \), \( \text{CD}_n^+ \); \( \square \), \( \text{CD}_n^+ \).](image)

The feature is that they all reach the same magnitude of \( 2 \times 10^{-16} \text{ cm}^2 \) once the initial rise from threshold is past. It is also noted that the appearance threshold has a monotonic increase with \( n \), though the thresholds for \( n = 3-5 \) are almost indistinguishable.

For \( n = 2 \) and \( 5 \), measurements have also been performed\textsuperscript{71,73} using a storage ring and detecting the complementary neutral to \( \text{D}^+ \) (CD and \( \text{CD}_n \) respectively). For \( n = 2 \), the measured cross sections are identical to those with crossed beams, indicating no detectable dissociative ionization that yields \( \text{D}^+ \), while for \( n = 5 \) the cross sections measured using the two techniques are the same up to about 26 eV and then diverge in a manner interpretable in terms of dissociative ionization as mentioned for \( \text{CD}^+ \).

The cross sections for obtaining \( \text{D}_n^+ \) fragments from DE of \( \text{CD}_n^+ \) were also measured\textsuperscript{72} with crossed beams and found to be about an order of magnitude smaller than for obtaining \( \text{D}^+ \) for \( n = 3-5 \), and to be too small to measure for \( n = 2 \). The limiting cross sections in this case are not the same for each \( n \), but instead they increase with \( n \).

As can be found in the experimental references, there are potential curves for some of the ions considered here, but there is – as far as we can determine – absolutely no theory for dissociative excitation of any of these ions.

![Figure 10: Cross section for dissociative ionization of \( \text{H}_2^+ \). Solid points are Ref. 17 with 90% CL of random error. The solid curve illustrates theoretical results from Ref. 79.](image)
stabilization may occur via a number of different paths. One such path results in RDE, and another leads to DR. Such compound states were invoked many years ago in explaining a puzzling number of low energy fragment ions from dissociative ionization of H$_2$. Invoking the states to explain observations of DE at energies lower than the minimum energy for a vertical transition in the case of a number of ions is fairly recent. We have already pointed to the example of HD$^+$ in Fig. 7.

Perhaps the most illustrative example of this process can be seen in Fig. 12, showing the results of measurements of DE of H$_2$H$^+$. The figure shows both channels, the first leading to H + He$^+$ and the second leading to H$^+$ + He. Only the second channel shows strong evidence of RDE. In this case the vertical threshold is near 30 eV where the second rise in the cross section is seen—this can be assumed to be direct DE. The resonant “bump” between about 9 eV and 20 eV is very obviously RDE, as the location and shape of the curve is very close to a similar “high energy”

Figure 12: Dissociative excitation of H$_2$H$^+$. \( \Delta \), H$_2$ was detected; \( \bullet \), He$_2$ was detected, Ref. 63. Solid line presents theoretical results for RDE, Ref. 84.

bump in the DR cross section. Thus, many of the same Feshbach resonances are involved and the two stabilization channels compete. In this case the DR channel apparently “wins out,” as the peak of cross section is about three times higher than the RDE peak shown in Fig. 12.

Also shown in the figure is the result of a calculation by Orel and Kulander for

3.4 Resonant Dissociative Excitation

Some of the neutral resonances involved in dissociative recombination may also be involved in RDE. After electron capture and formation of the compound state,
the same process. In their *ab initio* calculation, the electronic scattering parameters came from complex Kohn variational calculations and a quantum wave-packet treatment was used for the dissociation dynamics. The authors make some speculations about why their calculation gives a cross section a factor of 2 higher than the experiment. Not shown in the figure is their theoretical result that the heavier isotopes that move apart more slowly after formation of the compound state (thus giving more time for autoionization) have larger RDE cross sections as intuitively expected.

The other emphatically clear example of RDE occurs in the studies of Le Padellec et al., who made CRYRING measurements of DR and DE cross sections for D$_2$. Again, there is a very distinct peak in the cross section at an energy well below the vertical threshold and the peak position and general shape coincides beautifully with a corresponding peak in the DR cross section. Here, RDE wins out, with that cross section’s being about 2 times larger than that for DR. The cross sections for two DE channels are shown in Fig. 13. Only the channel giving D’ + D$_2$ shows RDE. Included in the plot and shown by the solid curve is the cross section for DR of D$_2$, in the same energy range, illustrating a close relationship of the two processes.

![Cross Section Graph](image)

**Figure 13:** Cross section for DE of D$_2$: * blend, D was detected; A, D$_2$ was detected. Solid line represents DR of D$_2$. Ref. 62

A “high energy” peak in the DR cross section is by no means, however, a guarantee that there will be an RDE peak in a given DE channel. For example, the DR cross section$^{73}$ for CD$_3$ has a distinct peak at about 10 eV, but there is no similar feature in the DE cross section$^{2,72}$ in the CD$_4$ + D’ channel (see Fig. 9). Of course an RDE peak could well appear in other dissociation channels of CD$_3$. This point is also made in Figs. 12 and 13.

Though, as indicated, the states leading to RDE have been recognized for some time, the RDE process itself has only recently been recognized. It is surely an additional important mechanism that must be accounted for in modeling of low temperature plasmas.

### 3.5 Resonant Ion Pair Formation

In fact, RIP [Process 1(d)] is another stabilization channel after dielectronic capture into the compound states or Feshbach resonances involved in DR and RDE. Thus, one might expect in electronegative gases to see cross sections for RIP that resemble the “bumps” seen in Figs. 12 and 13. As far as we know, there are only three published experiments$^{18,26,60}$ reporting measurements of cross sections for this process, two from the Newcastle group, and one from the Ontario group. All three deal with the fundamentally important hydric ions. For the measurements$^{18}$ on H$_2^+$ a “multiple pass” ion source at low pressure was used, the vibrational population distribution of von Busch and Dunn was characteristic of the ion target. Only fragment H$^+$ ions were detected, since RIP is the only way to form these ions at the energies involved, and inclined beams were used. Results of the measurement are somewhat nondescript, declining from a value 4.94 × 10$^{-18}$ cm$^2$ at 0.4 eV to a value 1.16 × 10$^{-18}$ cm$^2$ at 3.96 eV with a little inflection around 2 eV. The cross sections are roughly a factor of 5 less than a theoretical prediction of Dubrovskii and Ob’edkov,$^{85}$ but little can be made of this disagreement since the theory is for vibrational ground state ions. In general, the cross section has a similar appearance to DR for “hot” H$_2^+$. Figure 14 shows the data of Pearl and Dolder$^{18}$ as points and the theory of Dubrovskii and Ob’edkov$^{85}$ as the dotted curve. One of the more recent measurements$^{58}$ of DR for “hot” H$_2^+$ has been divided by 100 to put it on the same scale with RIP and is shown in the figure as the solid curve.

Again, for the measurements$^{26,60}$ of RIP for H$_3^+$, neither group used the coincidence method to identify the process. It was noted that they needed only to measure H$^+$ production to insure that they were seeing RIP. Results of their measurement are shown in Fig. 15. Also shown in this case is the RDE curve$^{62}$ from Fig. 13 for D$_2$ which has been divided by 56. The data for D$_2$ are shown, since there are no comparable RDE data for H$_3^+$. As expected according to the discussion, the curves are very similar in shape and position since they just represent different stabilization channels of the same resonances.
3.6 Halogen Molecular Ions.

Considering the interest in and importance of halogen-containing species for plasma etching and deposition, it is surprising that very little work has been done on these species. Since halogens are so strongly electronegative, one may expect that RIP may play a fairly large role.

At JILA Cl⁺ from electron-impact of Cl₂⁺ was detected and the cross sections for obtaining these fragments were measured.²⁴ To our knowledge these are the only such data for a halogen-containing molecular ion. The results are shown in Fig. 16. Despite the fact that at the lowest energies the uncertainties get unreasonably large, it is clear that the cross section is quite large even to very low energies well below the dissociation energy of the ion (D₀ = 3.95 eV). Again with some license of interpretation in view of the uncertainties and the number of points, there is some evidence of a maximum near 2.5 eV with a minimum near 5 eV. Whether the large cross section at energies below D₀ is due to RIP or to internal excitation of the target can only be speculated. Clearly experiments detecting Cl⁺ should be carried out and work with other halogen-bearing ions remains an important challenge.
4. Outlook

Practical applications of the data in the field of technology and other sciences have led to renewed interest in dissociating collision processes. This has been accompanied by the advent of new equipment and techniques that make it possible to obtain targets that are otherwise difficult to prepare. These developments have led to a new understanding of the processes involved, providing a basis for the development of new technologies and methodologies.

One of the most exciting developments in this area is the use of Rutherford Backscattering Spectrometry (RBS) to study the microscopic structure of materials. RBS is a powerful tool for investigating the atomic structure of materials, and it has been used to study a wide range of materials, from metals to ceramics.

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References


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